

Formation of Hydrate From Single-Phase Aqueous Solutions



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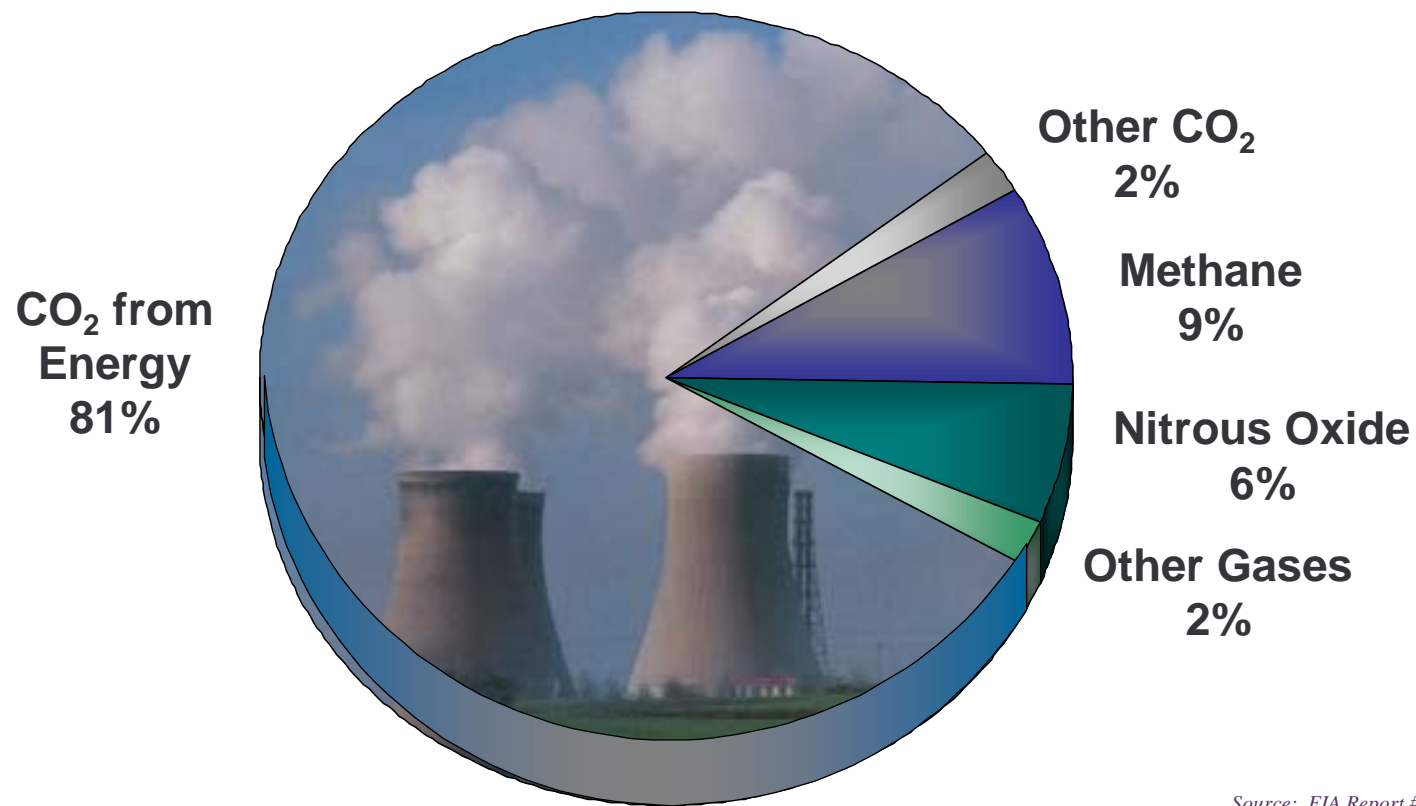
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CO₂ from Energy is a Major Contributor to Anthropogenic Greenhouse Gas Emissions

*U.S. GHG Emissions Weighted by Global Warming Potential
(Equivalent Global Warming Basis)*



Technological Carbon Management Options

Reduce Carbon Intensity

- Renewables
- Nuclear
- Fuel Switching

Improve Efficiency

- Demand Side
- Supply Side

Sequester Carbon

- Capture & Store
- Enhance Natural Sinks

All options needed to:

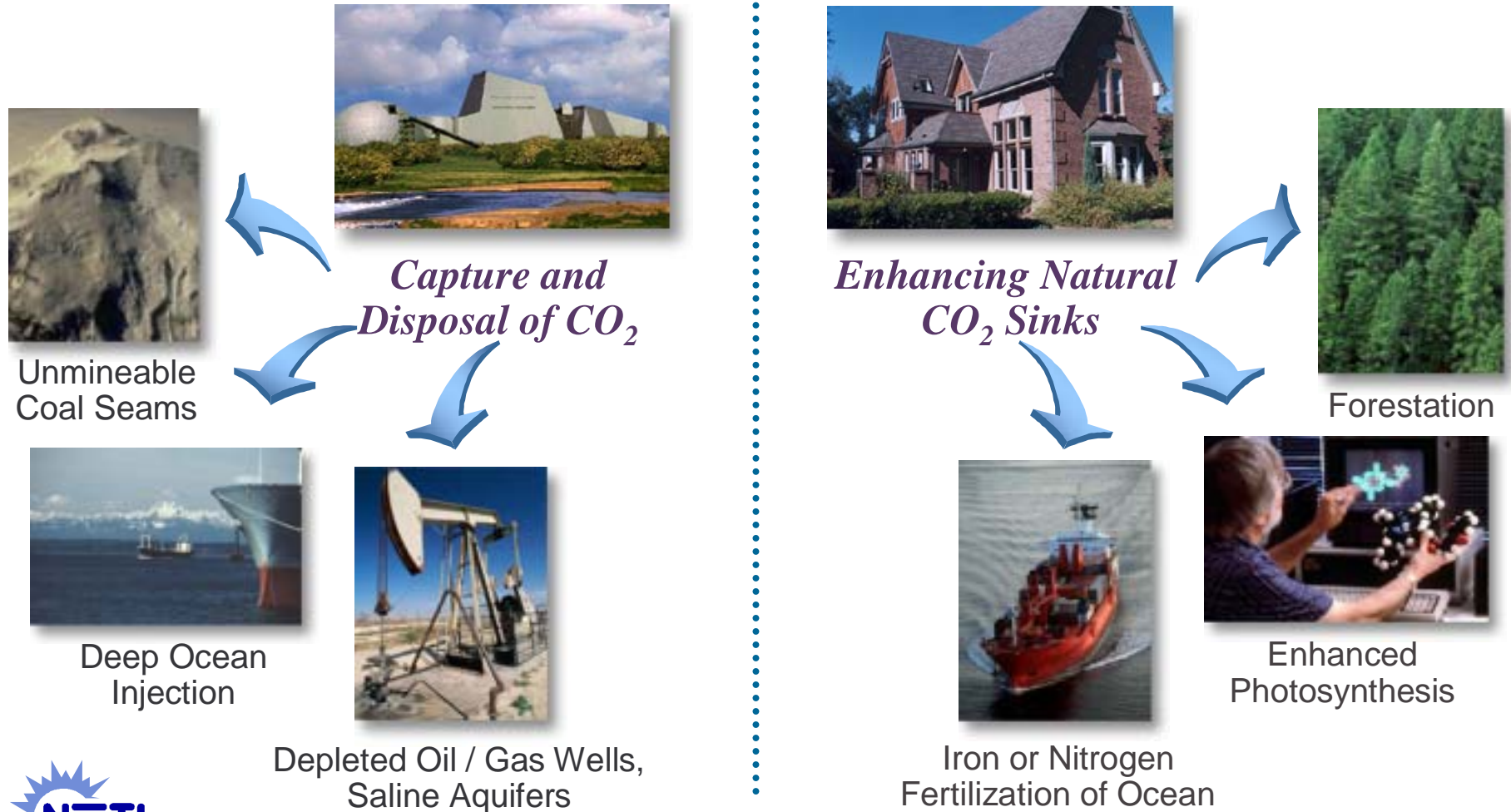
- Affordably meet energy demand
- Address environmental objectives



Types of Sequestration

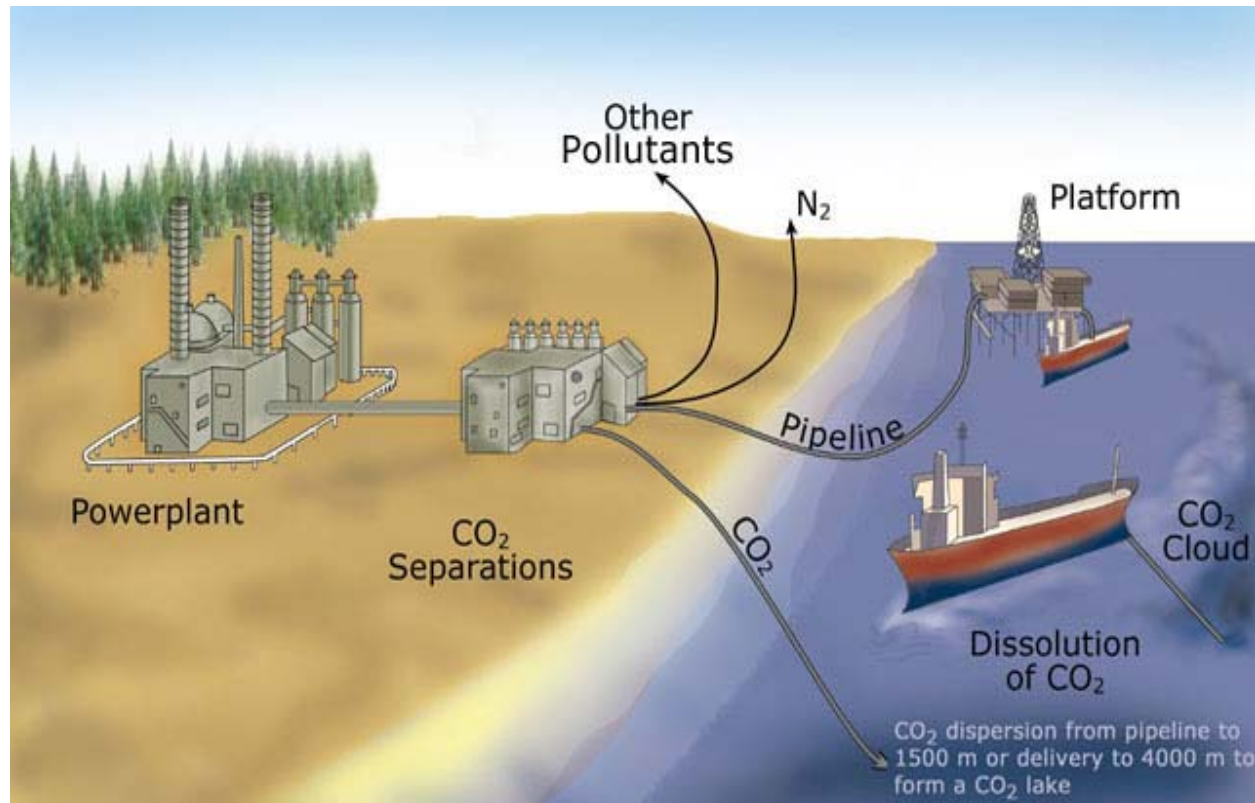
Direct

Indirect



Ocean Sequestration

- Direct injection of CO₂ into the ocean



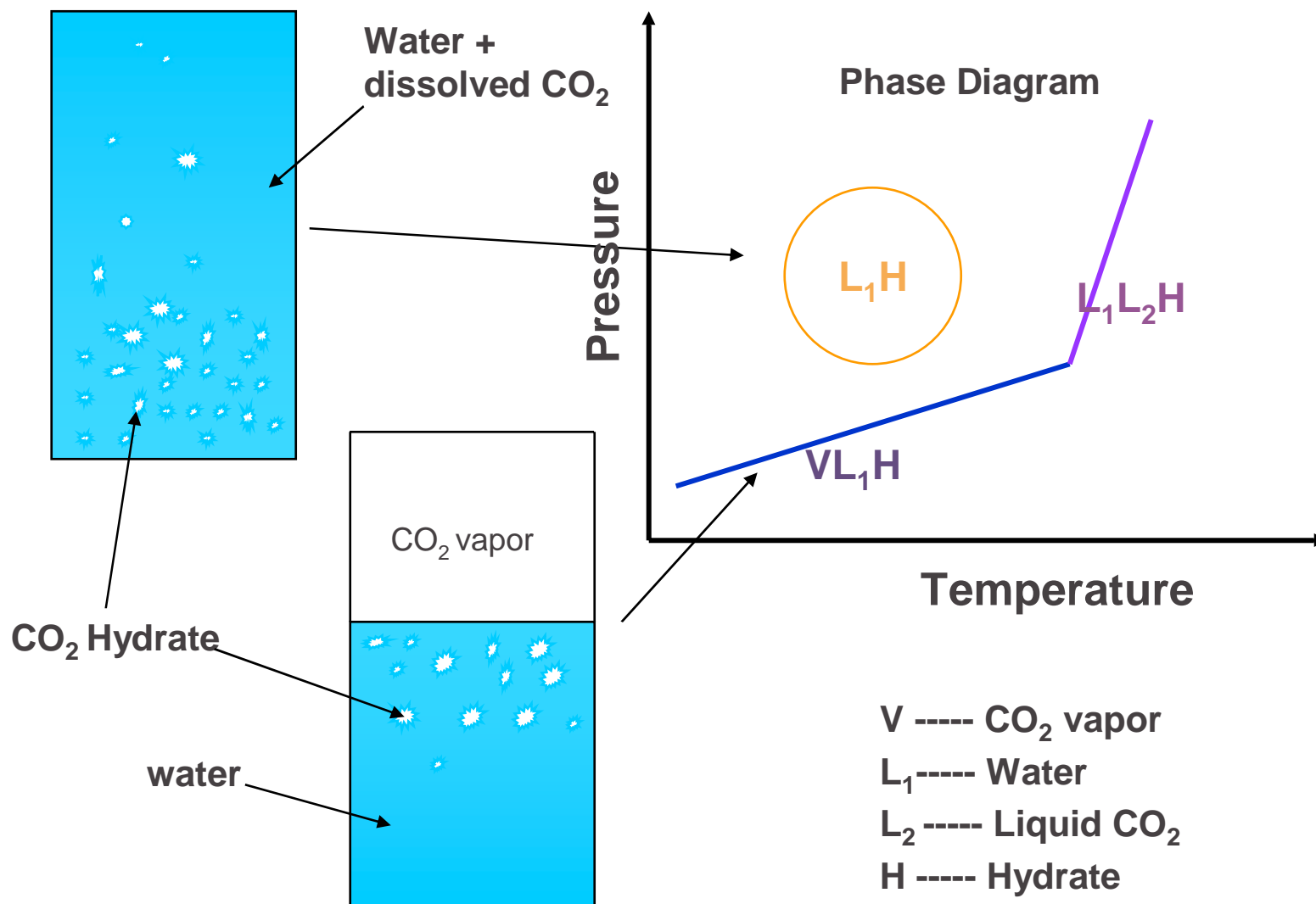
DOE Center for Research on Ocean Carbon Sequestration

Implications from Previous Research

- Physical and chemical behavior of CO₂ in the deep ocean, especially formation of CO₂ hydrate, will impact the sequestration process.
 - Hydrate formed from a two-phase system (liquid or gaseous CO₂ in contact with seawater) is initially less dense than seawater.
 - Rising hydrate particles reduce sequestration efficiency.
 - Greater injection depths required.
 - Hydrate formed from a single-phase system (CO₂ dissolved in seawater) is initially more dense than seawater.
 - Sinking hydrate particles enhance sequestration efficiency.
 - Longer CO₂ residence times.



Hydrate Formation from Single-Phase Solutions



Status of Current Research

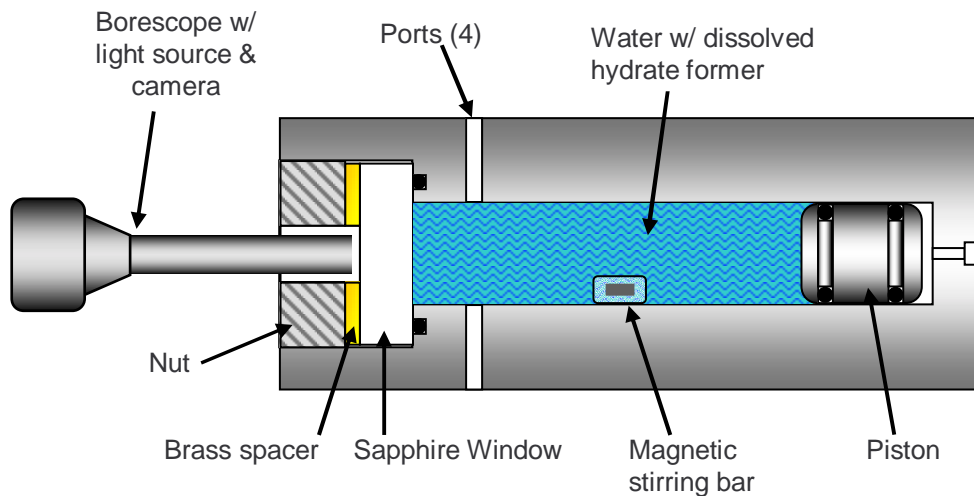
- **Fundamentals of hydrate formation**
 - Conducting experiments to validate thermodynamic model for predicting two-phase hydrate equilibrium (formation from single-phase aqueous solutions).
 - Modifying and improving theoretical model for prediction of single-phase hydrate formation.



High-Pressure, Variable-Volume Viewcell

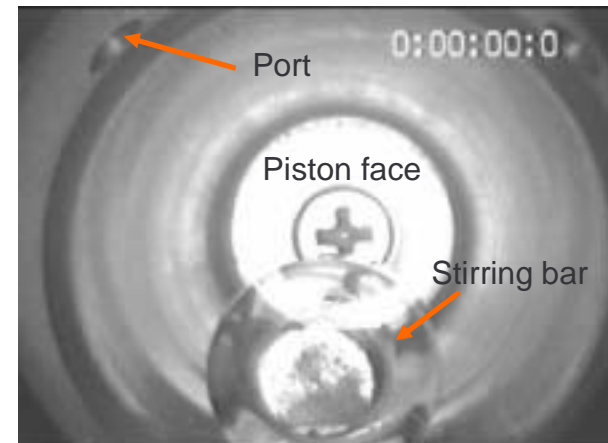
- **Features**

- Direct observation of systems from 243 K to 473 K (-30°C to 200°C) at pressures to 138 MPa (20,000 psig).
- System pressure easily changed via internal piston.
- Remote monitoring and recording of observations.



High-Pressure, Variable-Volume Viewcell

View through glass window



General Purpose Seawater (GPS) from Ocean Scientific International, Ltd. Cell at 5.8°C, 16 MPa.



High-Pressure Viewcell System



View showing syringe pumps, chamber, and computer monitoring and control system.

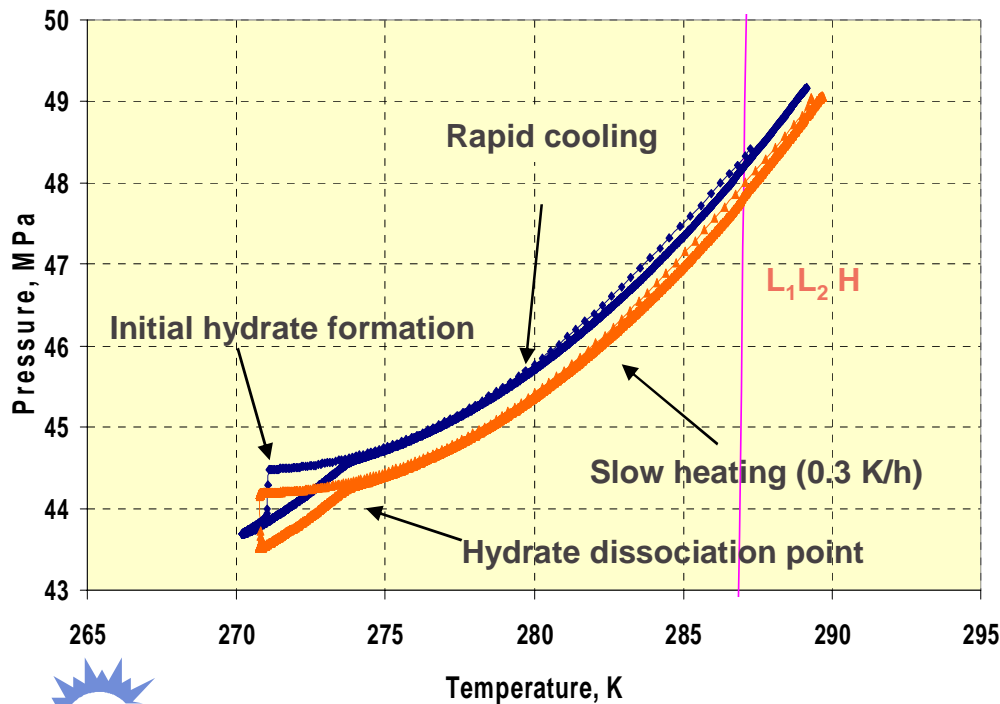
View showing viewcell in chamber and borescope placement.



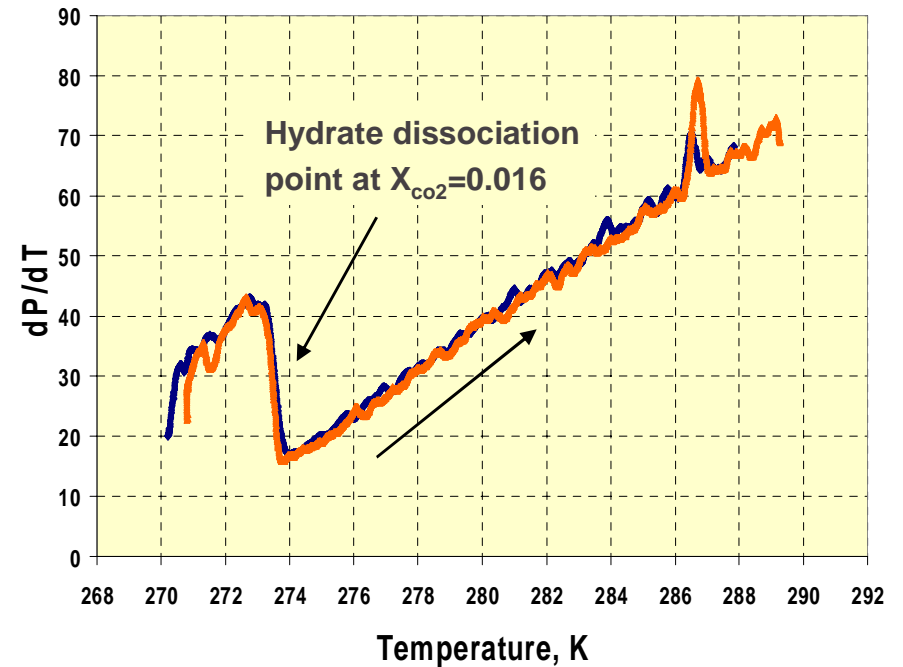
Experimental Data and Analysis

- Experimental results for two cycles at $X_{\text{CO}_2} = 0.016$ using 18 Megohm-cm water.

Pressure vs. Temperature



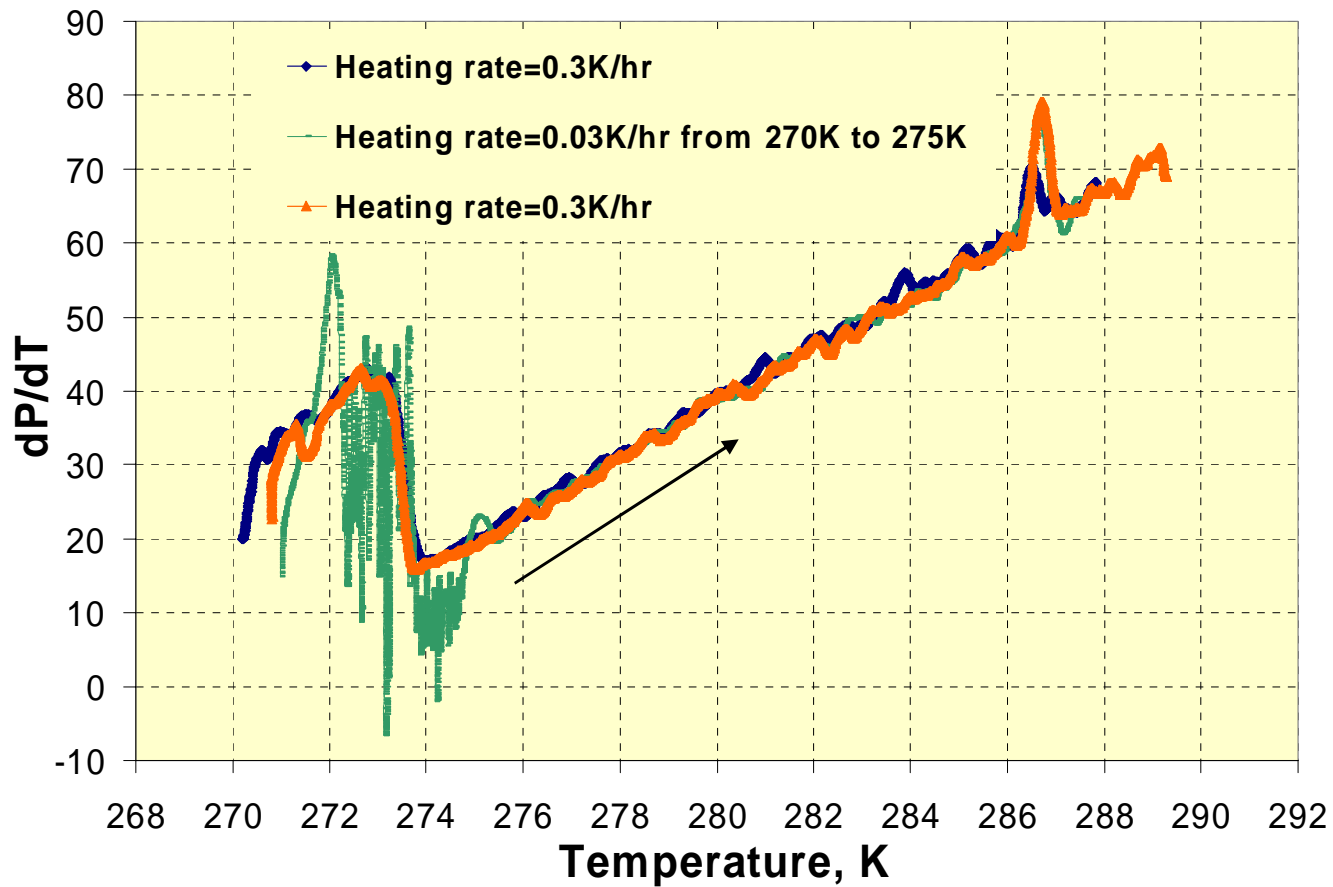
dP/dT vs. Temperature



- A derivative plot permits more accurate determination of the hydrate dissociation point.

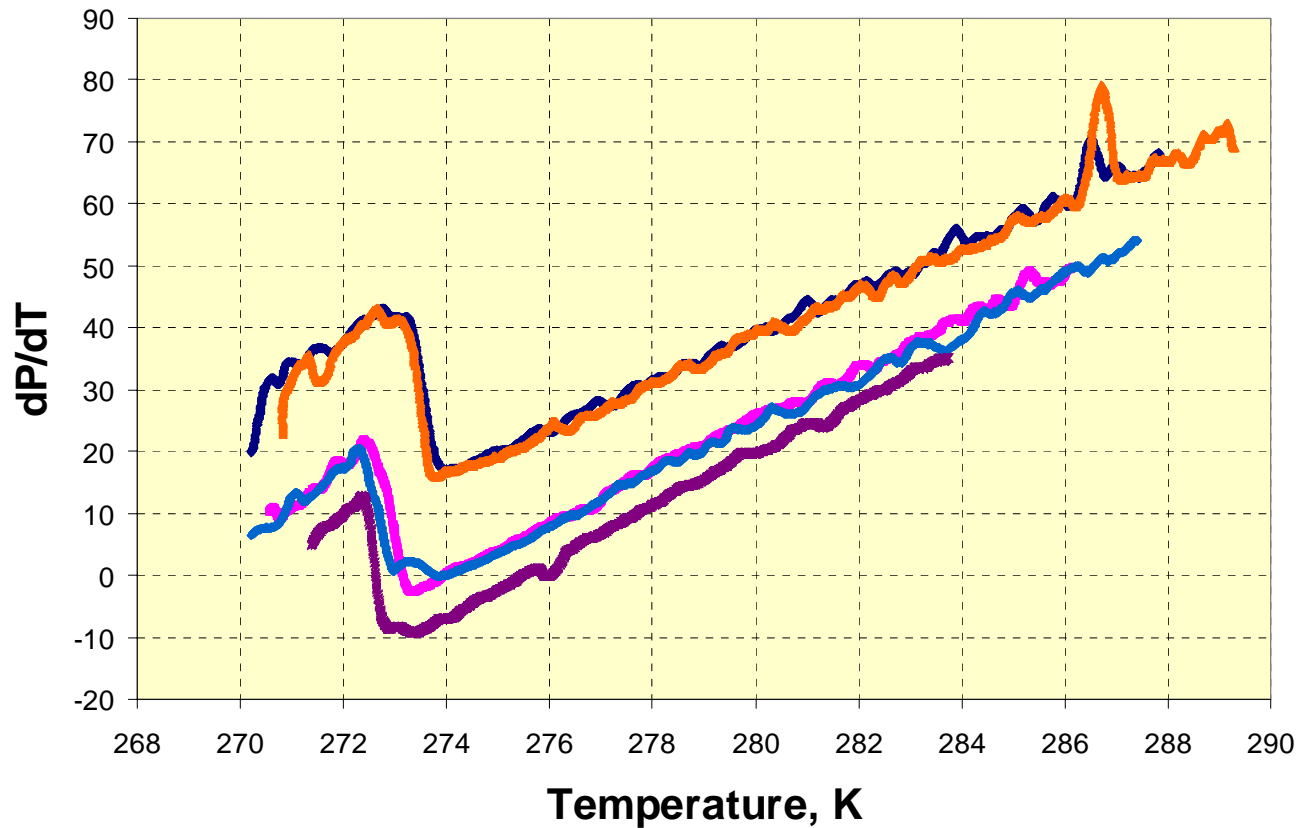
Examination of Heating Rate

dP/dT vs. Temperature at $X_{CO_2}=0.016$



Comparison at Different Pressures

dP/dT vs. Temperature at $X_{CO_2}=0.016$

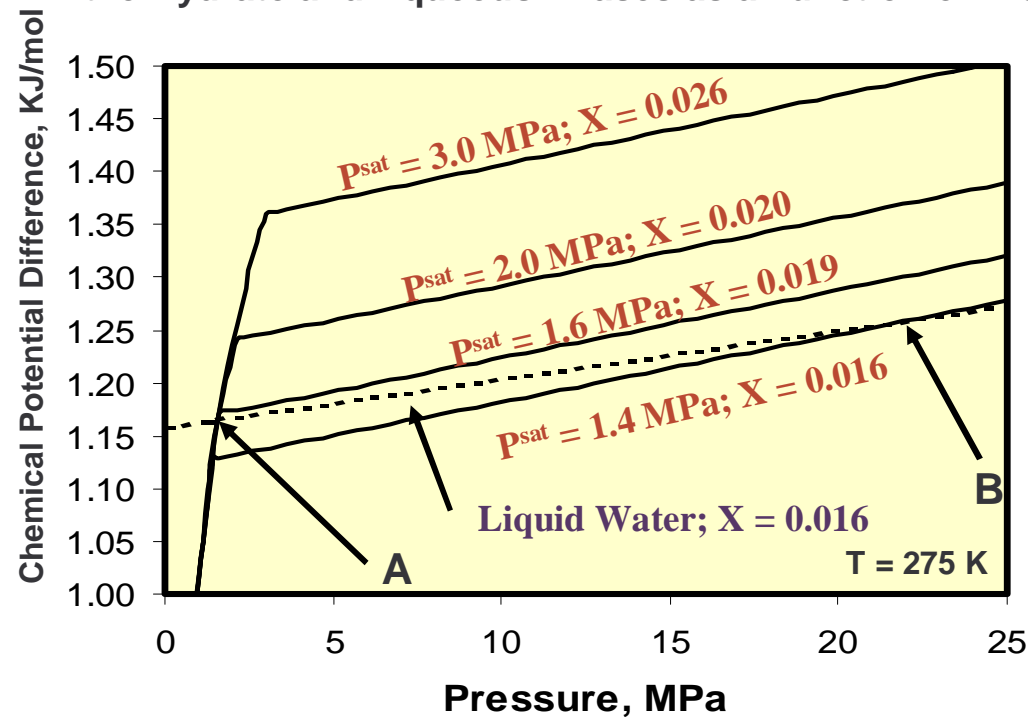


Prediction of Single-Phase Hydrate Formation

$$\frac{\Delta\mu_H}{RT} = - \sum_{j, \text{cavities}} \nu_j \ln \left(1 - \sum_i \theta_{ji} \right) \quad \text{where,} \quad \theta_{ji} = \frac{C_{ji} f_i}{1 + \sum_i C_{ji} f_i}$$

$$\frac{\Delta\mu_L}{RT} = \frac{\Delta\mu_L^o}{RT_o} - \int_{T_o}^{T_F} \frac{\Delta h}{RT^2} dT + \int_0^P \frac{\Delta v}{RT} dP - \ln X_w$$

Comparison of the Chemical Potential Difference of Water in the Hydrate and Aqueous Phases as a Function of Pressure



Modified Thermodynamic Model

- Hydrates form from single-phase solution, at fixed temperature

$$- \sum_{j, \text{cavities}} \nu_j \ln \left(1 - \sum_i \theta_{ji} \right) = \frac{\Delta \mu_L^0}{RT_0} + \int_0^P \frac{\Delta V}{RT} dP \quad (1)$$

- Hydrates form from two-phase solution, at fixed temperature

$$- \sum_{j, \text{cavities}} \nu_j \ln \left(1 - \sum_i \theta_{ji}^{VLH} \right) = \frac{\Delta \mu_L^0}{RT_0} + \int_0^{P^{VLH}} \frac{\Delta V}{RT} dP \quad (2)$$

- Subtract (2) from (1), for single hydrate species, we obtain

$$- \sum_{j, \text{cavities}} \nu_j \ln \left(\frac{1 - \theta_{ji}}{1 - \theta_{ji}^{VLH}} \right) = \int_{P^{VLH}}^P \frac{\Delta V}{RT} dP \quad (3)$$

Which gives the increase in pressure (over the VLH pressure) required to form hydrates.



Modified Thermodynamic Model (Cont.)

- Finally,

$$\sum_j \nu_j \ln \left[\frac{\frac{1}{C_{ji} f_i^{VLH}} + \frac{f_i^{sat}}{f_i^{VLH}} \exp \left(\frac{\bar{V}_i (P - P^{sat})}{RT} \right)}{\frac{1}{C_{ji} f_i^{VLH}} + 1} \right] = \frac{\Delta V (P - P^{VLH})}{RT} \quad (4)$$

- The approximations:

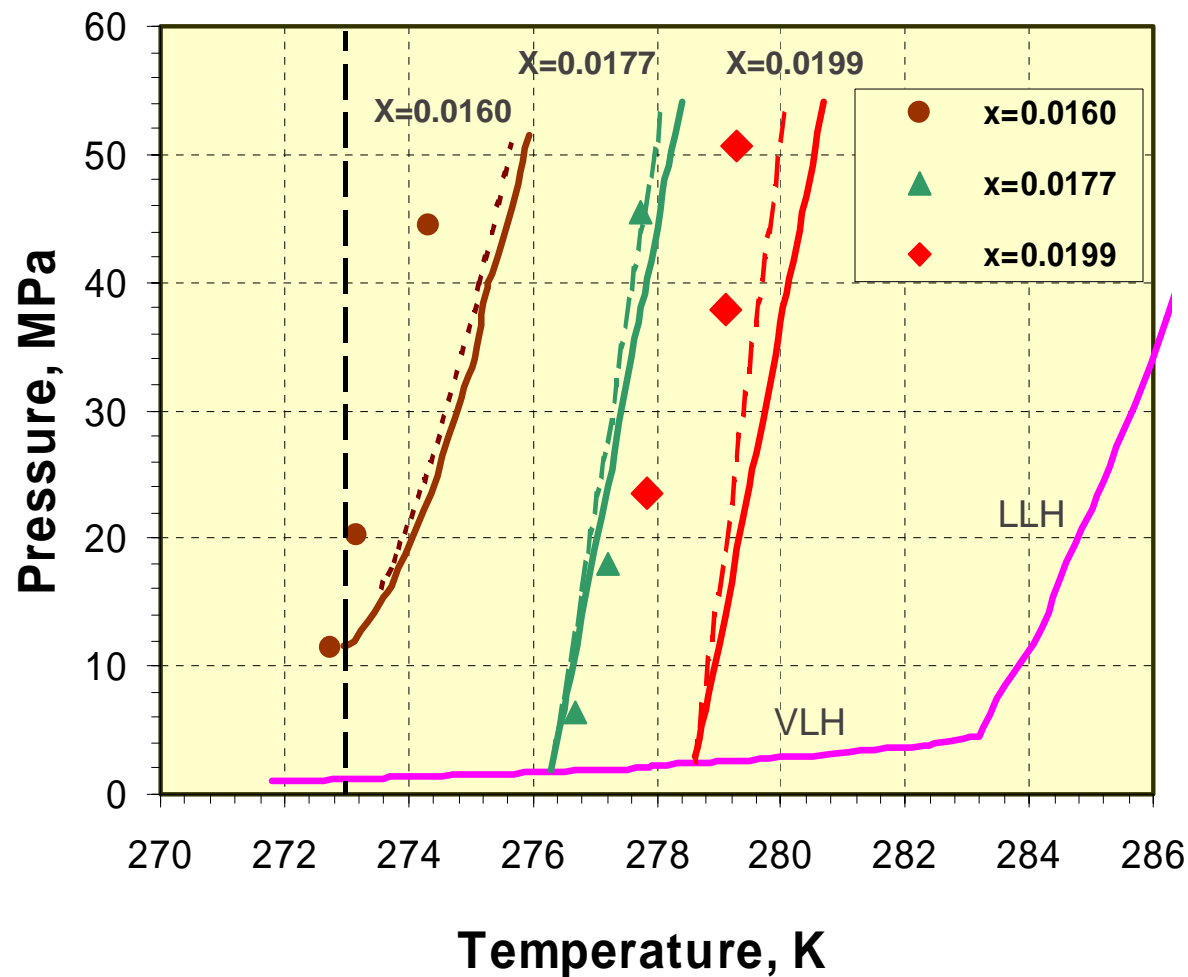
$$C_{ji} f_i^{VLH} \gg 1, \quad \frac{f_i^{sat}}{f_i^{VLH}} \approx \frac{P^{sat}}{P^{VLH}}$$

We obtain,

$$\sum_j \nu_j \ln \left[\frac{P^{sat}}{P^{VLH}} \exp \left(\frac{\bar{V}_i (P - P^{sat})}{RT} \right) \right] = \frac{\Delta V (P - P^{VLH})}{RT} \quad (5)$$



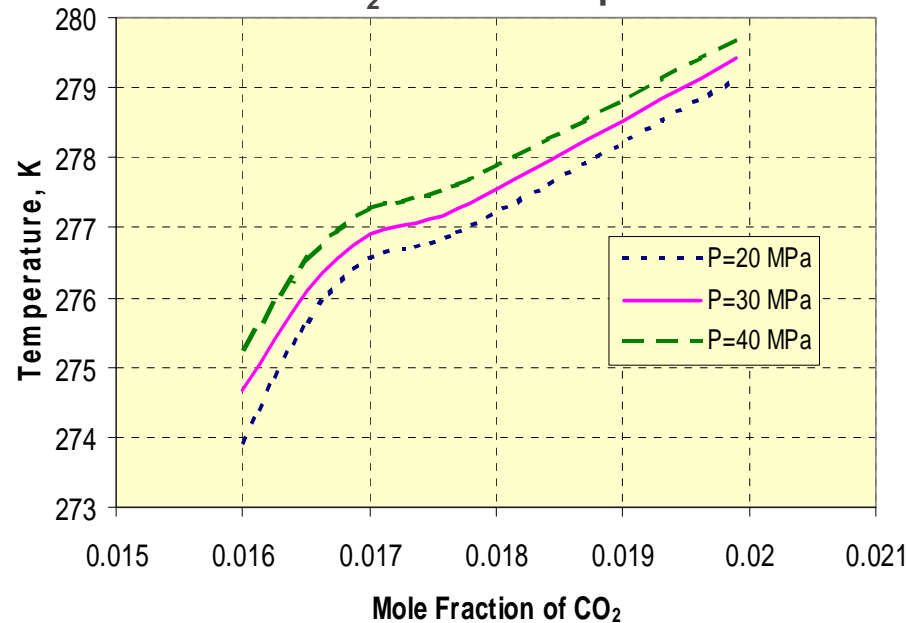
Comparison of Experimental and Predicted Data by the Modified Model



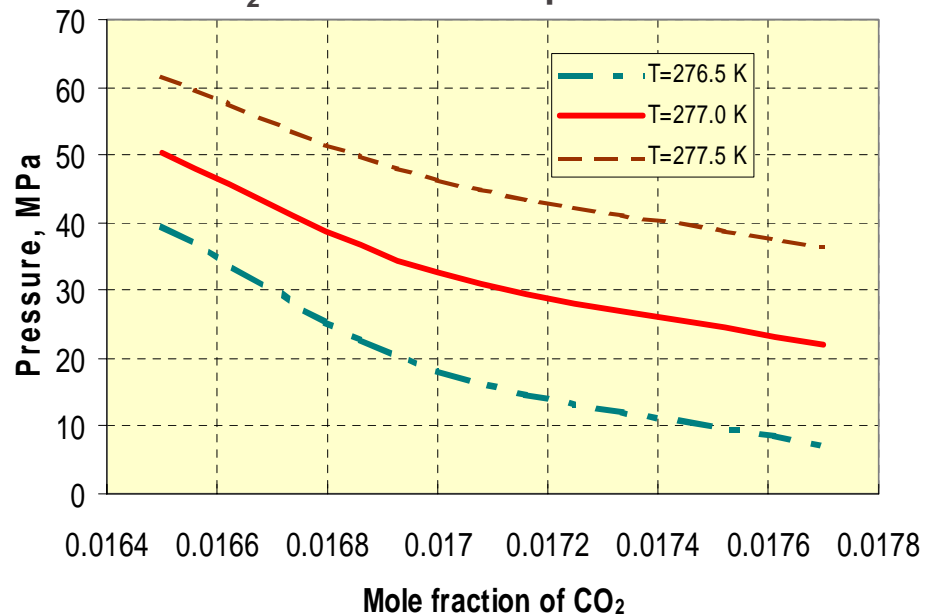
Vertical dashed line - $T=273.15$ K region. Solid lines - exact model; Dashed lines - simplified model

Other Theoretical Calculations

Hydrate equilibrium temperature vs. Mole fraction of CO₂ at constant pressure



Pressure vs. Mole fraction of CO₂ at constant temperature



Summary

- **Experimental procedures have been developed for determining the phase behavior of hydrate formed from single-phase aqueous solutions.**
- **A theoretical model is being developed to describe the behavior of hydrate formation from single-phase aqueous solutions.**
- **The results of this research will be useful in determining the efficiency and impacts of deep-ocean sequestration.**



Future Work

- **Theoretical**

- Combine “restricted rotation model” and “expanded cell model” to develop new models to provide a better understanding and prediction of the system.
- Incorporate the effect of seawater.

- **Experimental**

- Complete experiments in freshwater.
- Perform experiments in seawater.



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